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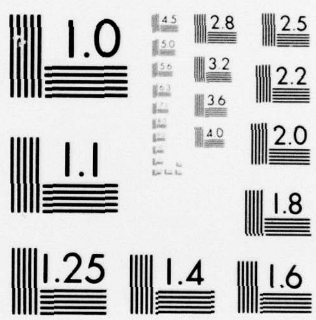
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SPECTROSCOPY IN KINETIC STUDIES OF GAS-PHASE REACTIONS

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Abstract

New developments in remote sensing, communications, energy systems and other areas of interest depend upon advances in laser technology. Chemical or transfer laser systems hold promise of fulfilling many of these needs. The development of new and better chemical laser systems, however, awaits increased understanding and knowledge of the reactive and spectral characteristics of candidate molecules. The research under this grant has concentrated on obtaining a detailed understanding of metal-oxidant and metal-halogen reactions. Photon yields and product state branching ratios have been determined for many reactions. In many cases it was necessary to develop basic spectroscopic information on the electronically excited product molecules. In the course of these studies, other molecules of atmospheric, combustion, or chemical laser interest also came under scrutiny, and molecular constants were obtained.

Various diatomic molecular species have been produced in vacuum flow systems; typically metal vapor entrained in an inert gas is reacted with a halogen or oxidant. These exothermic reactions produce product molecules in excited states whose fluorescence (chemiluminescence) is analyzed. Laser induced fluorescence (photoluminescence) is also used to probe both ground and excited electronic states.

The following research summary is organized according to experimental technique.

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1) Chemiluminescence, Photon Yields, and Branching Ratios

Reactions of lead with N_2O, O, O_2, and O_3 were investigated under a wide variety of conditions and were found to depend dramatically upon both oxidant species and pressure.[11] Addition of active nitrogen or NF_3 to the flame resulted in a strong enhancement of the PbO band intensity and introduced strong atomic emission while CO, NO, and N_2 quenched the flame. Many new bands were found and molecular constants were determined.

A method was devised to illustrate, on one graph, the population behavior of electronic and vibrational states as the flame conditions were changed. Unless both the electronic and vibrational state populations can be described by a single temperature (and satisfy Boltzmann statistics) the graph will be nonlinear. The technique does not require absolute measurements or knowledge of transition probabilities, but allows use of direct relative photomultiplier signals. The various oxidants used in the PbO experiment gave widely varying population distributions in the product molecule.

Modifications to the standard furnace system allowed extension of its upper temperature limit by several hundred degrees, to 2100 K, and permitted production of TiO.[14] O_2, N_2O, NO_2, NO, and CO_2 were used as oxidants of the titanium atoms; the first two species were chosen for detailed study. Ti + O_2 flames had electronic and vibrational temperatures of 2500 ± 500 K, while Ti + N_2O flames were approximately twice as hot, and exhibited wider departures from Boltzmann statistics. Ultraviolet emission was three orders of magnitude higher with N_2O than with O_2.

Confirmation of our matrix isolation determination[4] of the $a^1\Delta - X^3\Delta$ spacing as 3500 cm^{-1} was obtained from intensity data. Molecular constants of the $E^3\Pi$ state were determined. An anomalous feature in the TiO spectrum was attributed to YO contamination and preliminary work on a study of yttrium reacting with oxygen has commenced.

Preliminary photon yield data have been taken for the reactions of copper with F_2, NF_3 and SF_6. Chemiluminescence spectra of CuF have been taken in the 200-1100 nm region and corrected by computer for relative spectral response of the detection system. Three new electronic states have been discovered with transitions at 438, 568 and 680 nm; strong perturbations in the spectrum of the $A^1\Pi - X^1\Sigma$ transition are caused by the close proximity of the upper state in the new 568 nm transition. Total photon yields from 200-800 nm were less than 0.5% for the reaction Cu + F_2, and lower for Cu + NF_3; 60-90% of the emission was in the A-X transition, and 10-40% divided between the B-X and C-X systems.

Aluminum atoms diluted in a buffer gas were reacted with F_2, Cl_2, Br_2, I_2, NF_3, and SF_6 to produce diatomic aluminum halides in chemiluminescent flames.[13] Emission from $a^3\Pi$ to $X^1\Sigma^+$ was observed for all the halides, and for Al, AlF and AlCl, higher electronic states were also observed. Photon yields were 2% for Al + NF_3, and less than 0.01% for the other reactants. In the case of Al + NF_3, about 90% of the total yield was due to Al atomic emission and in fact the atomic emission extended up to the ionization limit at 207 nm. Energy transfer from metastable molecules was invoked as the excitation mechanism.

*References and talks, listed in chronological order, are found following section 9.

Observation of intercombination emission from AlF allowed the first direct determination of the $a^3\Pi - X^1\Sigma$ separation,[9] which agreed well with an earlier value calculated from vibrational perturbations observed in the $A^1\Pi$ state.

Emission from ultraviolet to near infrared was observed from flames of Al atoms reacting with various oxidants.[3] The species N_2O, O_2, microwave discharged O_2, O_3, CO_2, NO_2, NO and CO were used to form the AlO. Photon yields for the reactions varied widely from 3% for Al + microwave discharged O_2, and 2% for O_3, to 0.4% for N_2O and less than 0.005% for all other oxidants. The $A^2\Pi$ to $X^2\Sigma$ system, which had not previously been observed in emission, was seen with several of the oxidants. A broad band emission feature present with excess oxidant was attributed to further oxidation products of AlO.

An isotopic substitution experiment[10] of Ba reacting with $N_2{}^{16}O$ or $N_2{}^{18}O$ allowed unique absolute numbering of the vibrational states in BaO, and subsequent determination of the spectroscopic constants of the $A'^1\Pi$ state.

2) Photoluminescence

A single mode tunable dye laser was used to induce photoluminescence from CuF. High resolution scans near the origin of the $A^1\Pi - X^1\Sigma$ transition show strong perturbations from a newly discovered state at around 17600 cm^{-1}. This perturbation is exhibited as an extremely large Λ-type doubling of the $A^1\Pi$ state ($q \approx .01$ cm^{-1}).

Six wavelengths of the Ar^+ laser have been found to be coincident with transitions in Cu_2. Five of these lines ranging from 457.9 nm to 488.0 nm excite the $B^1\Sigma_u$ state, while the 496.5 line excites the $A^1\Pi$ state.

Laser induced photoluminescence has been observed from TiO molecules[15] produced in a chemiluminescent flame of Ti + O_2. Ar^+ and cw dye lasers were used in a detailed study of the $\alpha(C^3\Delta - X^3\Delta)$ system in emission. Techniques were developed for assigning photoluminescence transitions involving states of high multiplicity in molecules with several isotopes. Emission in the 0-0 band of the $\beta(c^1\phi - a^1\Delta)$ system, observed with 476.5 nm excitation, was shown to result from collisional relaxation of the $C^3\Delta(v{=}2)$ to $c^1\phi(v{=}0)$ states. Assignment of a new $C^3\Delta_3 - a^1\Delta$ transition places the $a^1\Delta$ state at 3444±10 cm^{-1} above the $X^3\Delta$ state, thus confirming and refining earlier measurements made in this laboratory of the singlet-triplet separation. These experiments have greatly improved the overall spectroscopic understanding of this astrophysically important molecule.

3) Lifetime Measurements

The radiative lifetimes have been measured for the $A^1\Pi$, $B^1\Sigma$ and $C^1\Pi$ states of CuF and have been found to be .5, $.7_x$, and 12 microseconds respectively. Tunable pulsed dye lasers were used for the measurements with either flashlamp (1 μsec duration) or nitrogen laser (1 nsec pulse duration) excitation. A computerized detection system was developed to enable signal averaged and wavelength scanned lifetime measurements to be made. A high resolution time-resolved spectroscopic study of the $A^1\Pi$ state presently in progress is expected to elucidate the detailed nature of this highly perturbed state.

Radiative lifetimes have been measured[12] for the A and B states of Cu_2. Using a N_2-pumped tunable dye laser, lifetimes of 30±15 nsec at a background argon pressure of .5 torr and 20±15 nsec at 10 torr were measured for the first three vibrational levels of the B state. The A state lifetime of the v=0 level is 70±15 nsec at .5 torr and 50±15 nsec at 10 torr.

4) Computer Analysis

During the period of this grant a dedicated computer data handling system was purchased through another funding source. This system has proved itself a great utility in correcting spectra for instrument response, and in comparing calculated to observed spectra.

In studies of the CuF, $A^1\Pi$ state, comparison of data to synthetic spectra revealed the necessity of using different B values for the Q vs the P and R branches to obtain suitable agreement, and thereby revealed the existence of a new state which was responsible through perturbations for the anomalies in the $A^1\Pi$ state.

Such comparison of synthetic and observed spectra also facilitates determination of rotational and vibrational temperatures in chemiluminescent flames.

5) Excitation Transfer

Combustion of Mg vapor in N_2O with He and CO_2 diluents in a low-loss laser cavity resulted in cw oscillation at 10.6 μm.[7,5] The pumping takes place via chemical reaction and subsequent electronic-vibrational (E-V) energy transfer. The first step, whose exotermicity ultimately drives the laser, is the formation of electronically excited MgO. A large proportion of this MgO^* is in states whose radiative decay is slow. In the presence of CO_2 the dominant mode of destruction of these metastable MgO^* molecules is believed to be collisional conversion of their electronic excitation to vibrational excitation of CO_2, with the consequent inversion of the (001) level with respect to the (100) level.

Further studies of this topic under support of AFOSR grant 76-2959 demonstrated that the population of MgO^* will react efficiently with CO to yield $Mg(^3P)$ atoms and excited CO_2.

High-lying Rydberg levels of Al were excited[8] in a chemical reaction with NF_3. A possible mechanism is that high lying levels of Al are populated by energy transfer from excited molecular nitrogen produced in the Al + NF_3 mixture. Al atomic states up to the series limit were observed with NF_3 as well as in another experiment with microwave discharged N_2. While with active nitrogen, the resulting populations of the Al excited states followed a Boltzmann distribution at about 3000 K, in the case of the NF_3 the population distribution was non-Boltzmann and skewed toward higher energies.

Active nitrogen was also used in experiments on TiO and PbO flames,[11,14] where it materially enhanced the molecular emission as well as causing intense atomic emission from the metal. In the case of Pb the effect was primarily to increase the electronic temperature while maintaining a Boltzmann distribution It is believed that PbO^* was produced by transfer from active nitrogen to PbO. Similar explanations apply in the case of TiO.

6) Gain Measurements

Intracavity laser gain measurements using a CO_2 electrical discharge probe laser were made to study flames of Ba, Ca and Mg burning in a mixture of N_2O, CO_2 and He.[5] Gain at 10.6 μm was detected for each of these metals. For the Mg flames the gain coefficient was found to be in the range of 10^{-3} - 10^{-2}/cm. The addition of N_2 diluent enhanced the gain, whereas CO diluent quenched it.

These measurements led to the observation of cw lasing as mentioned above.

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1.	J. M. Brom, Jr. H. P. Broida	Photodissociative Production of $O(^1S)$ and $N(^2D)$ From N_2O in an Argon Matrix at 4 K, Chem. Phys. Lett. 33, 384 (1975
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3.	S. Rosenwaks R. E. Steele H. P. Broida	Chemiluminescence of AlO, J. Chem. Phys. 63, 1963 (1975).
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9.	S. Rosenwaks R. E. Steele H. P. Broida	Observation of $a^3\Pi - X^1\Sigma$ Intercombination Emission in AlF Chem. Phys. Lett. 38, 121 (1976).
10.	J. C. Wyss H. P. Broida	Vibrational Analysis of the $A'^1\Pi$ State of Barium Oxide Using Two Isotopes, J. Mol. Spectros. 59, 235 (1976).
11.	C. Linton H. P. Broida	Chemiluminescent Spectra of PbO from Reactions of Pb Atoms J. Mol. Spectros. 62, 396 (1976).
12.	R. E. Steele	Photoluminescence, Lifetimes, and Discharge Excitation of Cu_2 J. Mol. Spectros. 61, 477 (1976).
13.	S. Rosenwaks	Chemiluminescent Reactions of Al Atoms and Halogens J. Chem. Phys. 3668 (1976).
14.	C. Linton H. P. Broida	Flame Spectroscopy of TiO: I. Chemiluminescence J. Mol. Spectros. xx, (in press 1976).
15.	C. Linton H. P. Broida	Flame Spectroscopy of TiO: II. Photoluminescence of the $\alpha(C^3\Delta - X^3\Delta)$ System, J. Mol. Spectros. xx, (in press 1976).

Talks and Presented Papers

1. 10-74 4th Conference on Chemical and Molecular Lasers, St. Louis, Missouri
"Chemiluminescence and Photoluminescence Spectroscopy of the Barium Monohalides" (R. S. Bradford, Jr.)

2. 10-74 4th Conference on Chemical and Molecular Lasers, St. Louis, Missouri
"The Diatomic Oxides and Halides of Ca and Sr: Photon Yields and $A^1\pi$ Molecular Constants" (G.A. Capelle)

3. 10-74 Physics Department Colloquium, University of California, Santa Barbara, CA.
"A Recent Visit to Laser Science in the Soviet Union" (H. P. Broida)

4. 10-74 Seminar, Stanford Research Institute, Menlo Park, CA.
"A Recent Visit to Laser Science in the Soviet Union" (H. P. Broida)

5. 11-74 Seminar, NBS Washington, D. C.
"A Recent Visit to Laser Science in the Soviet Union" (H. P. Broida)

6. 12-74 Physics Seminar, University of California, Santa Barbara
"An Attempt to Measure Atmospheric NO Density" (H. P. Broida)

7. 1-75 American Physical Society Meeting, Anaheim, CA
"Red ($A^2\Pi$-$X^2\Sigma$) System of the AlO Molecule", (R. E. Steele)

8. 2-75 University of Fredericton, New Brunswick Canada,
"Chemiluminescence and Photoluminescence of Diatomic Molecules" (H. P. Broida)

9. 3-75 University Federal de Penambuco, Department of Physics, Brazil
"Chemiluminescence and Photoluminescence of Diatomic Molecules" (H. P. Broida)

10. 3-75 University Federal de Penambuco, Brazil
"Flame Spectroscopy as a Research Tool" (H. P. Broida)

11. 3-75 University of Denver, Chemistry Department, Colorado
"Flames" (H. P. Broida)

12. 9-75 Second Summer Colloquium on Electronic Transition Lasers, Woodshole Mass.
"Sensing Chemically Excited Metastable Populations by CO_2 Laser Gain Measurements" (D. J. Benard)

13. 9-75 Second Summer Colloquium on Electronic Transition Lasers, Woodshole, Mass.
"Chemiexcitation Transfer from Metastable Molecules to Metal Atoms in Metal-Halogen Flames"
(S. Rosenwaks)

14. 10-75 Molecular Spectroscopy Meeting, UCSB, Santa Barbara, CA,
"A Summer of Frustration"
(H. P. Broida)

15. 11-75 Annual Meeting of the Division of Atomic and Molecular Physics, Canadian Association of Physicists, Fredericton, New Brunswick, Canada
"Optical Spectroscopy of Metal Atom Flames"
(H. P. Broida)

16. 12-76 American Physical Society Meeting, Stanford, CA
"Chemiluminescence and Photoluminescence of Gas Phase CuF"
(R. E. Steele, to be given).

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